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A Dataset for the Design of Smart Ion-Selective Electrode Arrays for Quantitative Analysis

Leonardo Tomazeli Duarte, *Member, IEEE*, Christian Jutten, *Fellow, IEEE*, Pierre Temple-Boyer, Ahmed Benyahia, and Jérôme Launay

Abstract—Smart sensors arrays (SSAs) provide a flexible approach to deal with the interference problem typical of ion-selective electrodes (ISEs). The development of the core of a SSA, the signal processing algorithm, often requires a dataset containing input-output measurements. Motivated by that, this letter presents a set of experiments with arrays of ISEs. The acquired dataset is publicly available in a web page where published results with these data can be added for benchmarking.

Index Terms—Chemical sensor arrays, dataset, ion-selective electrodes (ISEs), signal processing.

I. INTRODUCTION

ION-SELECTIVE ELECTRODES (ISEs) offer a simple way for estimating the ionic activity, a measure of effective concentration of an ion in aqueous solution [1]. However, ISEs usually lack selectivity, i.e., they may respond to interfering ions other than the target one. In a possible approach to deal with the interference problem, the data acquisition is performed by an array of sensors that are not necessarily selective. Then, in a second moment, signal processing tools are used for extracting the relevant information. This approach, which is known as smart sensor arrays (SSAs), has been widely applied on chemical sensing systems such as electronic tongues [2].

Recently, we considered quantitative analysis via smart ISE arrays based on blind source separation (BSS) methods [3]. Differently from the typical supervised solutions considered in ISE arrays, such as artificial neural network-based regressors, BSS methods operate in an unsupervised fashion, i.e., without requiring a training stage (calibration) prior to the effective use of the array. That is, the parameters of the SSA are adjusted based exclusively on the array outputs. For this to be possible, the ionic activities must present some temporal variation during the measurements and, moreover, some information on the source signals must be available [3].

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L. T. Duarte is with the DSPCom Laboratory, School of Electrical and Computer Engineering (FEEC), University of Campinas (UNICAMP), 13073-090, Campinas, SP, Brazil (e-mail: ltduarte@dmo.fee.unicamp.br).

C. Jutten is with the GIPSA-Lab (UMR CNRS 5216), Institut Polytechnique de Grenoble, 38404 Saint Martin d'Hères Cedex, Grenoble, France, and also with the Institut Universitaire de France, 75005 Paris, France (e-mail: christian.jutten@gipsa-lab.grenoble-inp.fr).

P. Temple-Boyer, A. Benyahia, and J. Launay are with the Laboratoire d'Architecture et d'Analyse des Systèmes (LAAS-CNRS), 31077 Toulouse Cedex 4, France (e-mail: pierre.temple-boyer@laas.fr; ahmed.benyahia@laas.fr; jerome.launay@laas.fr).

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Although BSS methods do not need a training database during its effective operation, it is still important that a set of input-output measurements be available during the development stage. Indeed, such a dataset allows one to obtain a parametric model for the array response, which is fundamental in BSS methods, and to assess the BSS algorithm. Therefore, whatever the adopted approach, it is important to have access to training datasets when developing signal processing algorithms for smart ISE arrays. Motivated by this observation and by the absence of publicly available datasets, we describe in this work a set of experiments with ISE arrays in three distinct scenarios. The obtained datasets are publicly available at www.gipsa-lab.inpg.fr/isea.

II. EXPERIMENTAL

The goal of our experiments is to acquire a dataset having basically the following entries: 1) activity of the ions under analysis and 2) the response of each ISE within the array.

A. Materials

Manufactured ISEs (Consort) were used in the experiments. Two titrators Dosimat 765 (Metrohm) were responsible for injecting solutions in a beaker. The solution under analysis was stirred through a Fisher Bioblock magnetic stirrer. The acquisition block was composed of a Consort C835 desktop analyzer and of an acquisition software developed by researchers of the LAAS-CNRS laboratory. All solutions were prepared using deionized water and, in contrast to common practice, no buffer solution to keep the pH fixed was used. The motivation for working in such a crude situation is related to the benefits brought by unsupervised SSAs, which reside exactly in the simplification of laboratory procedures.

B. Scenarios

The following three scenarios were considered.

- 1) Analysis of a solution containing NH_4Cl and KCl using one NH_4^+ -ISE, one K^+ -ISE and one Cl^- -ISE.
- 2) Analysis of a solution containing NaCl and KCl using two Na^+ -ISE, one K^+ -ISE and one Cl^- -ISE.
- 3) Analysis of a solution containing NaCl and CaCl_2 using two Na^+ -ISE and one Ca^{2+} -ISE.

The first scenario is a well-known example of interference between monovalent ions in ISEs. In the second one, the goal was to check if there is enough diversity within electrodes of the same type so the signal processing can take advantage of it. Finally, in the third scenario, we analyze the situation in which the ions have different valences. This is a difficult situation for BSS methods as the resulting mixing model becomes extremely nonlinear [3] in this case.

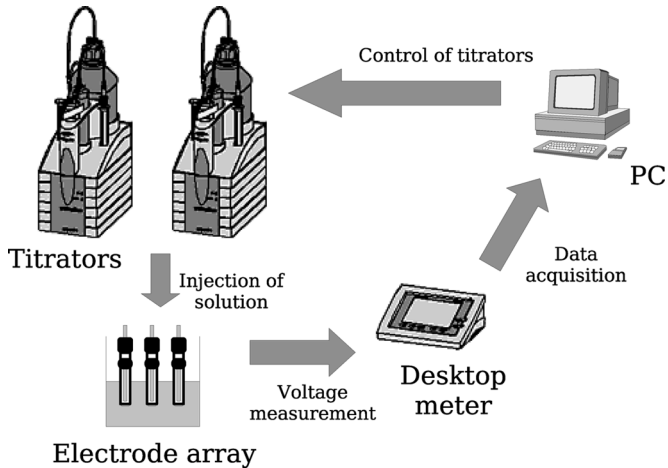


Fig. 1. Experimental setup.

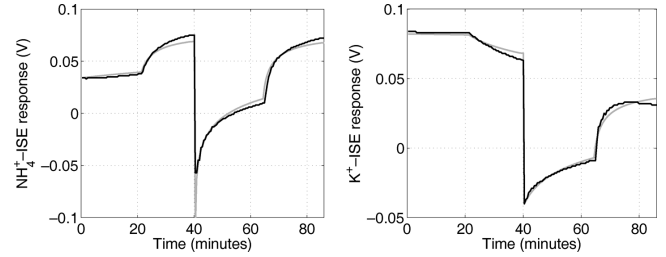
C. Experimental Details and Dataset Organization

In Fig. 1, a diagram illustrating the experimental setup is presented. As mentioned in Section II-B, for each scenario, there were two chloride salt solutions, represented here by $S_1\text{Cl}$ and $S_2\text{Cl}$, where S_1 and S_2 denote the cations associated with the chlorine anion. The concentrations of these cations were varied according to the following injection scheme: 1) initially, a solution of $S_1\text{Cl}$ with concentration C_i and volume $v = 50$ mL was set; 2) then, in a first period of approximately 1 h, only the first titrator was active and it injected the salt solution $S_2\text{Cl}$ (concentration 10^{-1} M) with an injection period of 30 s. The total injected volume was 5 mL; and 3) finally, in a second period of approximately 1 h, the first titrator was deactivated and the second titrator started the injection of the salt solution $S_2\text{Cl}$ (concentration 10^{-1} M). The total injected volume was 110 mL with an injection period of 30 s.

As a result of this injection scheme, the concentrations of the cations S_1 and S_2 vary in the range $10^{-4} - 10^{-1}$ M. Given that a linear injection scheme (same amount of solution at each injection) was considered, it became necessary to define two injection periods (steps 2 and 3) in order to obtain measurements in the concentration range $10^{-4} - 10^{-3}$ M. This explains why only 5 mL of solution is injected during the first hour of the experiment.

In each scenario, the same injection procedure was performed eight times (each realization took approximately 2 h), being the difference the initial concentration C_i of $S_1\text{Cl}$: we considered concentrations close to $C_i = 10^{-i}$ M, $i = 1, \dots, 4$. At the end of these four experiments, we repeated the same procedure but with an inversion of salt solutions, i.e., we started with an initial volume of solution $S_2\text{Cl}$ and then an injection of solution $S_1\text{Cl}$ took place. The electrodes were rinsed with distilled water between each experiment.

The following notation was defined to identify each experiment: $SAS_110^{-C}S_2$, where A, S_1 , C, and S_2 refer to the scenario number, the initial salt solution present in the beaker, its (approximate) concentration, and the injected solution, respectively. For example, $S1\text{NH}_410^{-1}\text{K}$ denotes an experiment of the first scenario where an initial solution of NH_4Cl with concentration of approximately 10^{-1} M was set, and where KCl was injected by the two titrators according to the procedure described above. Hence, the first scenario is composed of the following eight experiments: $S1\text{NH}_410^{-i}\text{K}$ for $i = 1, \dots, 4$ and

Fig. 2. Left: NH_4^+ -ISE response. Right: K^+ -ISE response. Electrode responses (black) and responses predicted by the NE model (gray).

$S1\text{K}10^{-i}\text{NH}_4$ for $i = 1, \dots, 4$. The activities were estimated through the Debye–Hückel formalism [1]

III. MODELING THE ISE ARRAY

The acquired data were modeled by the Nicolsky–Eisenman (NE) equation (see [1] for instance). A good fit between the NE equation and the data was observed when modeling each experiment of given scenario separately. However, when all the experiments of a same scenario were treated altogether, large regression errors were observed. This discrepancy points out that the NE equation could only provide a local description of the data. Indeed, modeling the whole data is difficult because of the lack of repeatability; the simple fact of immersing the electrodes in a new solution causes a considerable drift in the measurements. This was even more pronounced for the K^+ -ISE. It is worth mentioning here that the effects of drift can be mitigated in BSS-based solutions since these methods do not rely on calibration steps [3], only requiring an one-point calibration to retrieve the sources' scale. Conversely, in supervised solutions, a complete calibration stage should be done whenever the array's characteristic changes.

The highest interference level was observed in the first scenario. In particular, the more interesting situation to the study of sensor arrays¹ was given by the experiments $S1\text{K}10^{-1}\text{NH}_4$ and $S1\text{K}10^{-4}\text{NH}_4$. Indeed, in this case, both ISEs suffered from a relevant interference. The array responses obtained in these experiments are plotted² in Fig. 2. The modeling of this data through the NE model has led to a relative error of 6% for the NH_4^+ -ISE and of 1% for the K^+ -ISE.

IV. CONCLUSION

In this work, we described a set of experiments with ion-selective electrode arrays. The acquired data, which is publicly available, may be helpful in the development of signal processing algorithms tailored for smart ISE arrays.

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¹For instance, these experiments were considered in [3]

²Note here that the depicted responses are for time-varying ionic activities.